HIGH TEMPERATURE OXIDATION BEHAVIOUR OF NANOCRYSTALLINE $Fe_{80}Cr_{20}$ ALLOYS AND FERRITIC STEEL IMPLANTED WITH LANTHANUM AND TITANIUM

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ABSTRACT

Fe-Cr alloys and ferritic steel have received considerable attention as Solid Oxide Fuel Cell (SOFC) interconnects material. However, the main problem with the use of Fe-Cr alloys and ferritic steels as interconnect materials is their inadequate high temperature oxidation resistance. Chromium dioxide as the protective layers becomes non protective, due to formation of crack and volatile Cr_2O_3 upon exposure at high temperature oxidation. The prepared $Fe_{80}Cr_{20}$ alloy with smallest crystallite size expected to develop a protective film of Cr_2O_3 scales. On other hand, surface treatment via ion implantation technique can improve the oxidation resistance of alloys. Therefore, the purpose of this study is to investigate the oxidation resistance of implanted and unimplanted $Fe_{80}Cr_{20}$ alloy and available commercial ferritic steel in normal atmosphere over the temperature range of 1173-1373 K. Nanocrystalline $Fe_{80}Cr_{20}$ alloys have been produced by mechanical alloying process followed by hot compaction process. Lanthanum and titanium dopant were implanted into substrate of specimens with ion doses of $1x10^{17}$ ions/cm^2. Implanted and unimplanted of specimens were subjected to oxidation at 1173 K, 1273 K, and 1373 K for 100 h. Morphology characterization of oxide scales of specimens were investigated by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-Ray analysis (EDX). The results shows that $Fe_{80}Cr_{20}$ 60 h as the smallest crystallite size exhibit better oxidation resistance. The results also indicates that the implantation of lanthanum dopant effectively reduce the growth of oxide scale as well as increases the oxidation resistance.

ABSTRAK

Aloi Fe-Cr dan logam ferritic telah mendapat perhatian sewajarnya sebagai bahan penyambung dikenali Solid Oxide Fuel Cell (SOFC). Namun, masalah utama dalam penggunaan aloi Fe-Cr dan logam ferritic sebagai bahan penghubung ialah bahan tidak mencukupi ketahan pengoksidaan suhu yang tinggi. Kromium dioksida yang digunakan sebagai lapisan pelindung menjadi gagal bertindak sebagai pelindung kerana pembentukan rekahan dan pemeruwapan Cr_2O_3 kerana terdedah kepada suhu pengoksidaan yang tinggi. Tujuan kajian ini adalah untuk membangunkan struktur nanocrystalline baru pada aloi $Fe_{80}Cr_{20}$ yang dibandingkan dengan logam ferritic komersial, kemudian diteruskan dengan rawatan permukaan melalui teknik pengimplanan ion bagi penerapan pada suhu yang tinggi. Nanocrystalline $Fe_{80}Cr_{20}$ telah di hasilkan melalui proses pengaloian mekanikal diikuti dengan proses pemampatan. Dopan lanthanum dan titanium diimplan kepada substrat specimen dengan dos ion $1x10^{17}$ ions/cm^2. spesimen yang diimplan dan tidak diimplan didedahkan kepada pengoksidaan pada 1173, 1273 dan 1373 K selama 100 h. Skala oksida bagi karakter morfologi untuk specimen dikaji menggunakan X-Ray Diffraction (XRD) dan Scanning Electron Microscope (SEM) bersama-sama dengan analisis Energy Dispersive X-Ray (EDX). Hasil kajian menunjukan spesimen yang mempunyai saiz nano yang lebih halus ($Fe_{80}Cr_{20}$ alloy dengan masa pengisaran 60 jam) menunjukan prestasi yang terbaik dalam memperbaiki rintangan suhu pengoksidaan. Hasil kajian juga menunjukan implantasi lanthanum dopan berkesan untuk mengurangkan pertumbuhan skala oksida dan memperbaiki rintangan suhu pengoksidaan.

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LIST OF SYMBOLS AND ABBREVIATIONS

α	- Alpha
γ	- Gamma
λ	- Wavelength
θ	- Diffraction angle
ε	- Strain
ΔG	- Gibbs energy
ΔW	- Mass gain change
σRp	- Longitudinal straggling
A	- Surface area
a_1	- The lattice parameter of the pure solvent element
a_2	- The lattice parameter of solute element
a_{ss}	- The lattice parameter of solid solubulity and *x* is the solid solubility
$B_{corrected}$	- The instrumental corrected full width at half maximum (FWHM)
B_{inst}	- FWHM of the standard reference materials
$B_{observed}$	- The full width at half maximum (FWHM) from diffraction peaks of the specimens
Cr	- Chromium
Cr_2O_3	- Chromium dioxide
CT	- Cycle Time
D	- Crystallite size
d	- Interplanar spacing
EDX	- Energy-dispersive X-ray spectroscopy
Fe	- Iron
Fe_2O_3	- Iron oxide
$Fe_{80}Cr_{20}$ 7 h	- 80wt%Fe and 20wt%Cr with milling time 7 hours
$Fe_{80}Cr_{20}$ 15 h	- 80wt%Fe and 20wt%Cr with milling time 15 hours

$Fe_{80}Cr_{20}$ 20 h - 80wt%Fe and 20wt%Cr with milling time 20 hours

$Fe_{80}Cr_{20}$ 40 h - 80wt%Fe and 20wt%Cr with milling time 40 hours

$Fe_{80}Cr_{20}$ 60 h - 80wt%Fe and 20wt%Cr with milling time 60 hours

$Fe_{80}Cr_{20}$ 80 h - 80wt%Fe and 20wt%Cr with milling time 80 hours

FWHM - Full width at half maximum

ICDD PDF-2 - International standard diffraction data

K - Scherrer constant

k_p - Parabolic rate constant

La - Lanthanum

$LaCrO_3$ - Lanthanum chromite

LaB_6 - Lanthanum Hexaboride

MT - Milling time

pO_2 - Oxygen partial pressure

PT - Pause time

Rp - Ion range

S - Time oxidation (hours)

SEM - Scanning Electron Microscope

SOFCs - Solid oxide fuel cells

t - Time

Ti - Titanium

UTHM - Universiti Tun Hussein Onn Malaysia

W_0 - Mass before oxidation

W_t - Mass after oxidation

x_i - The depth penetration of implanted ions

XRD - X-Ray Diffractometer

YSZ - Yttria stabilised zirconia

CHAPTER I

INTRODUCTION

In this chapter, the background and premise of the research will be explained which consists of the research background focusing towards the research study, problem statement, hypothesis, research aim, objective study, scope and the significance of the research.

1.1 Research background

Fuel cells are devices that produce electrical energy through electrochemical processes, without combusting fuel and generating pollution of the environment. They represent a potential source of energy for a wide variety of applications (Ion & Loyalka, 2007). The basic physical structure of fuel cell consists of an electrolyte layer in contact with an porous anode and cathode on either side. In typical a fuel cell, gaseous fuels are fed continously to the anode (negative electrode) and oxidant (i.e. oxiygen from air) is feed continously to the cathode (positive electrode), electrochemical reactions take a place at the electrodes to produces an electrical current (Hirschenhofer *et al.*, 1998).

1.1.1 Types of fuel cells

At present, there are five main types of fuel cells according to different electrolyte materials. They are the polymer electrolyte fuel cell (PEFC), the phosphoric acid fuel cell (PAFC), the molten carbonate fuel cell (MCFC), the alkaline fuel cell (AFC) and the solid oxide fuel cell (SOFC). The main characteristics of these fuel cells are summarized in Table 1.1.

Although AFC is the oldest fuel cell and it provides extremely high power density, it is considered to be impractical because of the need to remove trace CO_2 from both the fuel and oxidant streams in order to prevent reaction of the electrolyte to form solid, non-conducting alkali carbonates. Furthermore the strong alkaline solution presents a number of problems. PAFC is the most advance fuel cell at the present stage. The high manufacture cost, however, prevents its commercialization. PEFC has recently attracted significant attention as a potential source of primary power in transportation application and worldwide investment in PEFC continues to grow. Given their high temperatures of operation, MCFC has great applicability in stationary power generation. But it suffers from the difficulties of containing a corrosive liquid electrolyte. In particular, dissolution of NiO at the cathode and its precipitation in the form of Ni at the anode can result in electrical shorts across the electrolyte (Yamamoto, 2000; Ormerod, 2003; Haile, 2003). Although in public eyes, SOFC is not as prominent as PEFC, it has many advantages such as multi-fuel capability and simplicity of system design. Moreover, the exhaust heat can be used as a heat source for a variety of processes (Yamamoto, 2000).

Table 1.1: The main characteristics of different types of fuel cells (Haile, 2003)

Parameter	Fuel cells type				
	AFC	PEFC	PAFC	MCFC	SOFC
Temperature K	333-393	343-353	493	923-1023	1073-1273
Electrolyte	KOH	Solid Polymer	Phosphoric acid	Lithium	Solid oxide
Fuel	Pure H_2	H_2	H_2	H_2, CO, CH_4	H_2, CO, Hydrocarbon
Efficiency %	33-55	30-40	40	>50	>50
Max power (kW)	5	250	200	1000	1000

1.1.2 Solid oxide fuel cells

Among various types of fuel cell, solid oxide fuel cells (SOFCs) has attracted considerable interest as it offers wide application ranges, the solid oxide fuel cells seem the most efficient way to generate electricity from a variety of fuel such as hydrogen, methane or even natural gases owing to their high operating temperatures typically in the range 1073-1273 K for conversion of chemical fuels directly into electrical power (Singhal & Kendal, 2003; Quadakkers *et al.*, 2003).

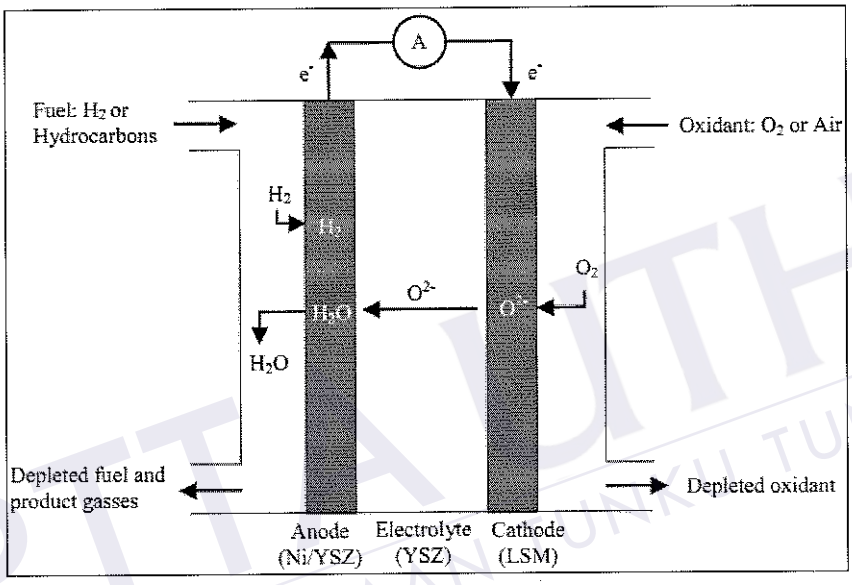

Figure 1.1: SOFC principles of operation (Stambouli & Traversa, 2002)

A solid oxide fuel cell is made up of four layers, three of which are ceramics. A single cell consisting of these four layers stacked together is typically only a few millimeters thick. Hundreds of these cells are then connected in series to form what most people refer to as an "SOFC stack". Figure 1.1 shows an SOFC scheme. It contains a solid oxide electrolyte, where in typically made from a ceramic such as yttria-stabilised zirconia (YSZ) which acts as a conductor of oxide ions. Ni-YSZ cermets are the most commonly used anode materials for SOFCs. Ni is an excellent catalyst for fuel oxidation. Conducting perovskites are the preferred cathode materials. Lanthanum manganite ($LaMnO_3$), which, when substituted with low valence elements such as Ca or Sr, has good type electronic conduction. Moreover,

doped $LaMnO_3$ possesses adequate electrocatalytic activity, a reasonable thermal expansion match to YSZ, and stability in the SOFC cathode operating environment (Singhal & Kendal, 2003). Since a single cell only produces voltage less than 1 V and power around 1 W/cm^2, many cells are electrically connected together in a cell stack to obtain higher voltage and power (Singhal, 2007).

Several technical issues have been identified and are being addressed in the development of SOFC products for practical applications. These issues mainly relate to competitive cost and reliable performance with desired operating characteristics. The development of suitable low cost materials and the low cost fabrication of material structures, with the aim of obtaining a higher and more stable electrochemical performance are presently the key technical challenges facing SOFC's (Singhal, 2000; Quadakkers *et al.,* 2003).

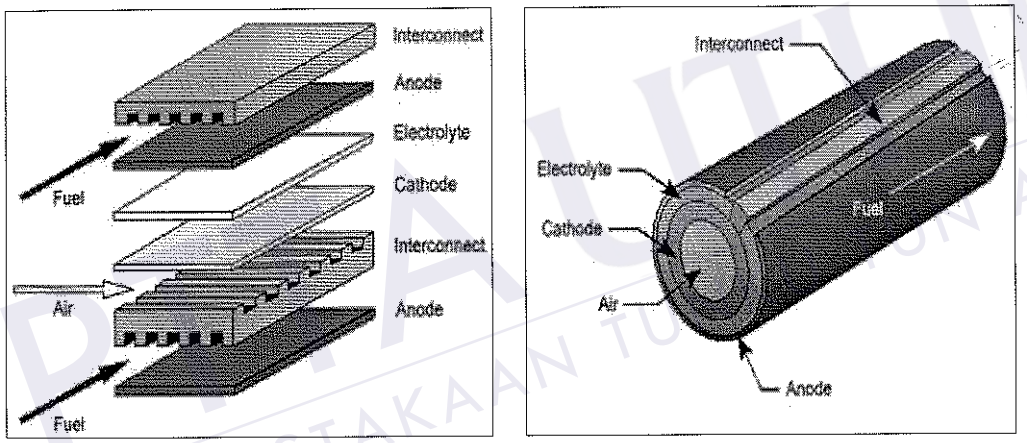

Figure 1.2: Planar and Tubular design of solid oxide fuel cell (Singhal, 2004)

Construction of the planar and tubular types SOFC require application of an interconnector to join the anode of one cell with the cathode of the next cell in a voltage stack as shown in Figure 1.2. For these reasons, the interconnector is a key element for the functioning and long-term reliability of SOFC.

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